



Study on a new single flow acid Cu–PbO₂ battery

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ABSTRACT

The present paper reports a new single flow acid battery, Cu–H₂SO₄–PbO₂ battery, in which smooth graphite is employed as negative electrode, lead dioxide as positive electrode and the intermixture of H₂SO₄–CuSO₄ as electrolyte. The reaction $\text{Cu} \rightleftharpoons \text{Cu}^{2+}$ takes place on the negative electrode. The working process of the battery is only the circulation of H₂SO₄–CuSO₄ intermixture by means of a single pump. No cationic membrane is needed. A miniature acidic copper single flow battery with a rated capacity of 2000 mAh can offer a discharge voltage of 1.29 V, an average coulombic efficiency of 97% and an energy efficiency of 83% during 450 cycles at a charge/discharge current of 1000 mA.

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1. Introduction

The flow energy storage battery is labeled as the ideal one among the new storage systems such as the pumped-storage power stations, compressed-air energy storage systems, super-capacitors, lead–acid batteries, and the sodium–sulphur fused batteries [1,2]. The flow batteries have developed fast in the recent years owing to their especial advantages [3]. The concept of the iron/chromium flow battery was first put forward by Thaller [4]. The early iron/chromium flow battery could supply operating voltage of 1.1 V with the oxidation–reduction reactions of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Cr}^{2+}/\text{Cr}^{3+}$. However, an obvious defect of this system is that severe cross-contamination emerges between Fe^{3+} and Cr^{2+} through ion exchange membrane, thus reducing charge/discharge efficiency and shortening the service life of the costly ion-exchange membrane [5,6]. The newly developed all-vanadium redox flow battery employs $\text{V}^{4+}/\text{VO}_2^+$ and $\text{V}^{2+}/\text{V}^{3+}$ as positive and negative electrode reaction substances respectively and supplies a discharge voltage of 0.9–1.2 V. Since the positive and negative electrode reactions take place between vanadic ions of different valences, theoretically speaking, cross-contamination will not happen between positive and negative electrode ions. With the efforts of researchers, a considerable progress has been made for vanadium flow batteries. However, the properties of vanadium flow batteries still need improving. It has been universally acknowledged that the all-vanadium flow batteries mainly have the following disadvantages: (1) The utilization of vanadium compound and ion-exchange

membrane leads to a higher price of the battery system and the voltage efficiency is reduced by membrane voltage. (2) The application of two liquid storage tanks and two pumps to store and transport electrolyte results in a rather heavy equipment system and leads to a low energy efficiency of 60–70%. Therefore, the abolishment of ion-exchange membrane and improvement of energy efficiency have become an investigation focus of flow batteries [7–10].

Recently, Prof. Pletcher proposes a new kind of lead–acid flow battery system, in which only one reactant exists and no membrane is needed [11–14]. However, it is a pity that the energy efficiency is still low, only around 65% [15].

Lead–acid batteries have been playing an active role for a long history of 150 years. Due to introduction of some modern technologies, lead–acid batteries are still ranked first in the battery family for broad application in motor vehicles, pumped storage stations and electro-mobility. It is recently reported that the newly developed lead–acid battery has achieved 4500 cycles life and has been applied to the accumulators in Californian power stations. However, lead–acid batteries can only keep the energy efficiency of 65–70% owing to the severe side reaction of negative electrode in the charge process. Additionally, it is difficult to develop a large scaled lead–acid battery due to the dimensional limitation of positive and negative electrode slabs [16,17].

Based on the properties of existing flow batteries [18–21] and lead–acid batteries, a novel single flow battery, Cu–H₂SO₄–PbO₂ battery, is proposed herein (see Fig. 1). This battery employs smooth graphite as copper negative electrode on which reaction $\text{Cu} \rightarrow \text{Cu}^{2+}$ takes place, lead dioxide as positive electrode and the intermixture of H₂SO₄–CuSO₄ as electrolyte. The reaction is expressed as follows:

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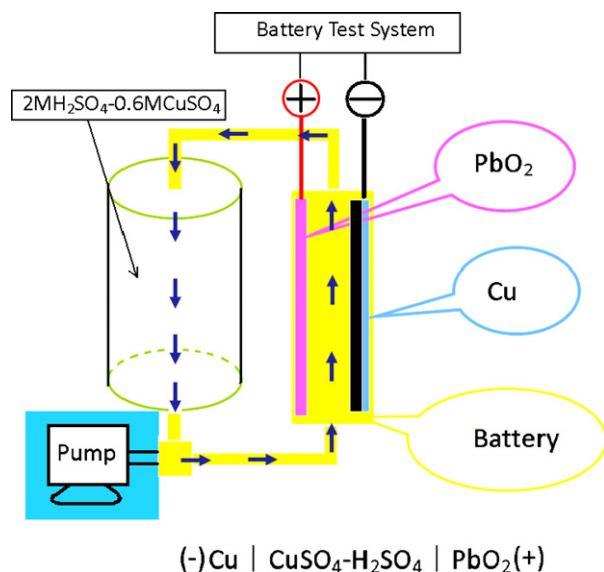


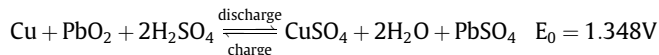
Fig. 1. Schematic diagram of single flow acid Cu–PbO₂ battery.

Positive electrode: $\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \xrightleftharpoons[\text{charge}]{\text{discharge}} \text{PbSO}_4 + 2\text{H}_2\text{O}$

$$E_0^A = 1.685\text{V}$$

Negative electrode: $\text{Cu} - 2\text{e}^- \xrightleftharpoons[\text{charge}]{\text{discharge}} \text{Cu}^{2+}$ $E_0^A = 0.337\text{V}$

Overall battery reaction:



The working process of the battery is only the circulation of H₂SO₄–CuSO₄ intermixture by means of a single pump and no cationic membrane is needed. The results reveal that a miniature single flow acid copper battery with a rated capacity of 2000 mAh provides a discharge voltage of 1.29 V, an average coulombic efficiency of 97% and an energy efficiency of 83% at charge/discharge current of 1000 mA during 450 cycles.

2. Experimental section

400 mL mixed solution was prepared with 60 g CuSO₄ · 5H₂O, 42.6 mL H₂SO₄ (98%) and deionized water. The solubility of CuSO₄ rises with increasing temperature. If the working temperature of battery is increased to 45 °C, 1 M CuSO₄–1.9 M H₂SO₄ solution can be prepared.

The experimental battery is constructed with high purity graphite as negative electrode and lead dioxide as positive electrode. The composition of the positive electrode is: PbSO₄/PbO₂ 98%, carbon fiber 1.2%, Sb₂O₃ 0.5%, and SnO₂ 0.3%. One slab of negative electrode was sandwiched by two slabs of positive electrodes. The inter-electrode distance was 2 cm. The size of negative and positive electrodes was 4 × 6 × 0.3 cm³ and that of electrolytic cell was 6 × 7 × 8 cm³ without any membrane barrier. 155 ml electrolyte was injected into the battery and 245 ml electrolyte was stored in the liquid storage tank. The electrolyte was circulated between the cell and the tank by a peristaltic pump with a flux of 500 ml/h.

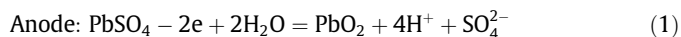
The galvanostatic charge–discharge tests were carried out with a LAND CT2001A battery test system (Jinnuo Wuhan Corp., China) at room temperature. In the charge–discharge cycles, the cell was

charged at 1000 mA (20.8 mA cm^{−2}) for 2 h and discharged down to 1.1 V at the same current density.

3. Results and discussion

Fig. 2a and b shows the typical curves of the charge/discharge capacity and energy, respectively, for the single flow acid copper battery at a high current of 1000 mA.

The reactions on both cathode and anode during charging are as follows:



Along with charge proceeding, Cu²⁺ is consumed and H₂SO₄ concentration is increased continuously. According to Faraday Law, 0.037 mol CuSO₄ is consumed and 0.074 mol H₂SO₄ is formed when a charge electrical quantity of 2000 mAh passes through. Therefore, 15.4% CuSO₄ is consumed after each charge process, which is regenerated in the succedent discharge process, thus keeping the electrolyte composition stable.

It can be seen that to discharge at the same current density after charging for 2 h, the battery presents a quite flat discharge curve between 1.33 V and 1.10 V and provides a discharge capacity of 1994 mAh and a capacity efficiency of 99.7% (Fig. 2a). Further results obtained through the analysis by testing software show that the average charge voltage of this battery is 1.493 V and the average discharge voltage is 1.274 V. In combination with its capacity efficiency, the energy efficiency of the battery reaches 84.3% in

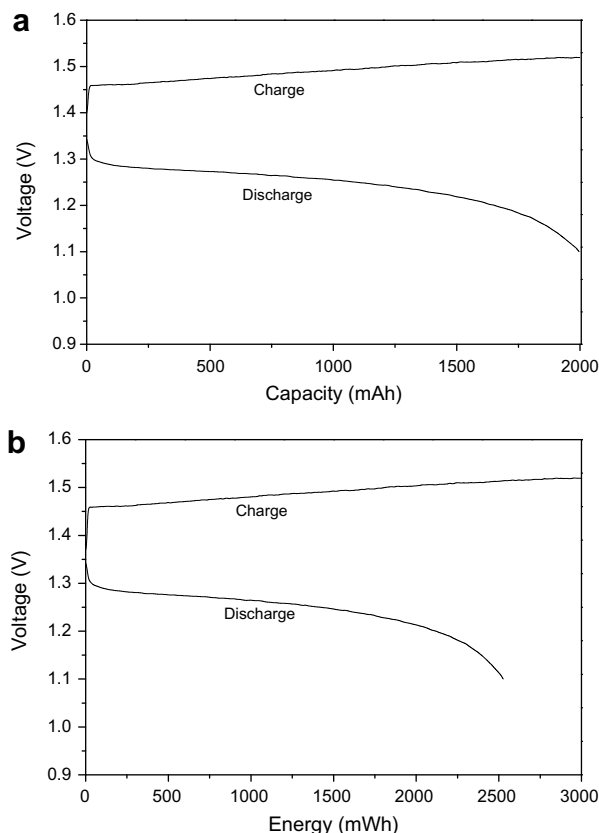


Fig. 2. The charge/discharge curves of single flow acid Cu–PbO₂ battery. (a) Charge/discharge capacity curve; (b) Charge/discharge energy curve electrolyte: 0.6 M CuSO₄–1.9 M H₂SO₄. The cell was charged at 1000 mA (20.8 mA cm^{−2}) for 2 h and discharged down to 1.1 V at the same current density.

the charge/discharge process (Fig. 2b), displaying fine charge/discharge capacity efficiency and energy efficiency of this battery system. When the charge/discharge current decreases from 1500 mA to 1000 mA, the energy efficiency increases from 83.1% to 85.4% on account of the reduction of polarization in the charge/discharge process.

To clearly depict the effect of positive and negative electrodes on charge/discharge, the charge/discharge performance of single electrode was investigated by employing a saturated $\text{CuSO}_4/\text{Cu}(\text{Hg})$ reference electrode of the same solution. Since lead dioxide has a fine charge/discharge performance in acid conditions, we chose a smooth graphite electrode as copper electrode on which reaction $\text{Cu} \rightleftharpoons \text{Cu}^{2+}$ took place and studied its individual charge/discharge process. For the ideal electrochemical equilibrium system, the reversible potential of a copper electrode is equal to that of another copper electrode in the same solution and does not change during charge/discharge process. Actually, the potential always slightly deviates from the ideal reversible potential. Fig. 3 is the charge/discharge curves of the above-mentioned copper electrodes. The potential deviation is considered as over-potential. In Fig. 3, the red horizontal line of zero potential is the potential of the Cu/Hg reference electrode. It is indicated in the experiment that this copper electrode displays good reversibility in the mixed electrolyte of $\text{H}_2\text{SO}_4\text{--CuSO}_4$. A slight voltage difference of only 0.13 V occurs between charge and discharge on the electrode. The fine electrochemical property is attributable to the fast charge/discharge reaction of metallic copper and copper ion in acidic solution. Compared with the charge/discharge voltage difference of 0.22 V for the copper fluid battery (Fig. 2a), it can be inferred that charge/discharge potential difference on PbO_2 electrode is approximately 0.06–0.09 V. The charge/discharge experiment also shows in Fig. 3 that the major polarization of the battery occurs on the negative electrode. With the increase in cycle numbers of charge/discharge, the corresponding efficiency of copper electrode rises gradually from 97.1% for the first cycle to 98.5% for the fourth one.

Fig. 4 exhibits the change in coulombic efficiency of the single flow copper battery with a rated capacity of 2000 mAh in the first 450 cycles. Generally, the deposition of Cu^{2+} on inert electrode does not form dendritic crystal. That is why this principle is broadly used in the electrolysis refining of copper. The copper deposited cathodically is almost totally dissolved in electrolyte in the succedent discharge process and the smooth graphite substrate is exposed again. As is shown by the results, the charge/discharge capacity of the flow copper battery keeps steady between 1941.3 mAh and 2003.1 mAh, meaning that the performance of the battery hardly decays during the 450 charge/discharge cycles, meanwhile, the capacity efficiency retains 97% and energy efficiency retains 83%. On the

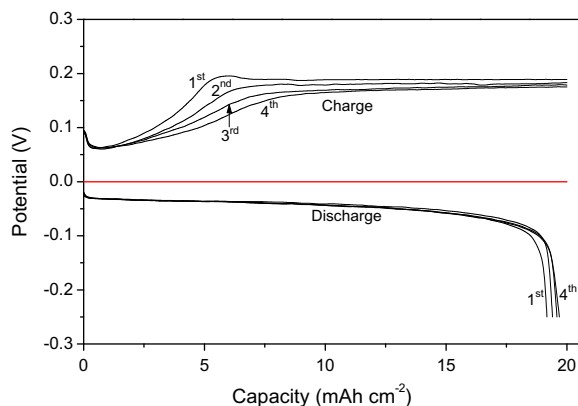


Fig. 3. The charge/discharge curves of the copper electrode on smooth graphite for single flow acid $\text{Cu}\text{--PbO}_2$ battery (Electrolyte: 0.6 M $\text{CuSO}_4\text{--}1.9$ M H_2SO_4 , current density: 20 mA cm^{-2}).

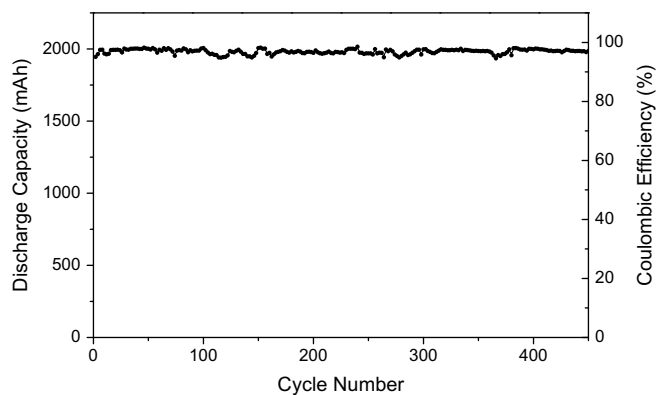


Fig. 4. Coulombic efficiency of the single flow copper battery in the first 450 cycles.

one hand, the superior charge/discharge performance is attributed to the proper oxidation-reduction potential of copper electrode where $\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$ is the only reaction and it is hard for H^+ and Pb^{2+} to discharge. On the other hand, since the strategy of surplus lead dioxide is adopted in the experiment, the charge/discharge extent of lead dioxide electrode is controlled to 50%, which guarantees an optimal current efficiency and avoids the damage to lead dioxide electrode caused by full scale charge/discharge, thus a longer cycle life of lead dioxide electrode is achieved. The high energy efficiency of single flow copper battery contributes to economizing electric energy and improving storage efficiency.

It can also be found in the experiment that a small quantity of copper powder and lead dioxide powder drops in the electrolytic cell. The fall of these electrode active substances accounts for the loss of battery's charge/discharge capacity. Moreover, in order to achieve higher cycle efficiency, only 15–32% of Cu^{2+} and 47–51% of PbO_2 are involved in electrode reaction, which indicates that the capacity of the fluid copper battery still has space of exploitation. The emphasis of the future research will focus on improving the utilization ratio of copper and lead dioxide electrode, enhancing physical characteristics of electrode surface and seeking for the optimal electrolyte composition and operating condition.

4. Conclusion

A new type single flow battery of safety and long life for distributional energy storage has been developed, in which the low cost PbO_2 is employed as positive electrode, depositional copper as negative electrode active substance and the flowing $\text{H}_2\text{SO}_4\text{--CuSO}_4$ solution as electrolyte. The problems of dendritic crystal, deformation and passivation are solved through electrolyte circulation. The property of the battery scarcely decays during 450 cycles of charge/discharge. It offers a discharge voltage of 1.29 V, an average coulombic efficiency of 97% and an energy efficiency of 83%. It is expected to be an ideal pattern of low cost and proper performance for the energy storage of power generation with renewable energy resources. It is a novel battery system worthy of deepening study.

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